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PREPARATION AND CHARACTERIZATION OF NICKEL SUBSTITUTED  
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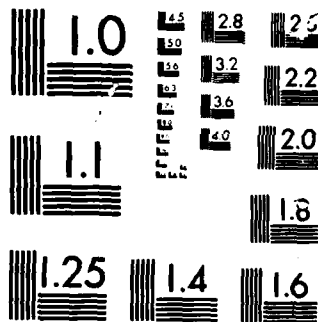
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Preparation and Characterization of Nickel Substituted  $\text{Fe}_5\text{C}_2$

by

Z-D. Zhang, R. Kershaw, K. Dwight and A. Wold

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Brown University  
Chemistry Department  
Providence, Rhode Island 02912

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## PREPARATION AND CHARACTERIZATION OF NICKEL SUBSTITUTED $\text{Fe}_5\text{C}_2$

Z-D. Zhang, R. Kershaw, K. Dwight and A. Wold  
Chemistry Department, Brown University  
Providence, Rhode Island 02912

### ABSTRACT

Nickel can be substituted into  $\text{Fe}_5\text{C}_2$  to the extent of 20 atomic percent. Samples were prepared by codecomposition of mixed nitrates followed by reduction at  $290^\circ\text{C}$  in a 9:1  $\text{H}_2:\text{CO}$  atmosphere. Confirmation of the limit of substitution was made by both magnetic and x-ray analysis.

MATERIALS INDEX: Magnetic analysis, Iron-nickel carbide

### Introduction

It has been shown by a number of investigators (1-4) that the catalytic activity of iron catalysts, used to reduce CO by hydrogen, was related to the extent of carbide formation. Fournier et al. (5) reported that the phases  $\text{Fe}_5\text{C}_2$  and Fe were detectable both from x-ray diffraction patterns and from thermomagnetic curves taken from products which were quenched after 10 minutes of reaction time (at maximum activity). It was shown that the active catalysts formed from both  $\text{Fe}_2\text{O}_3$  and metallic iron contain  $\text{Fe}_5\text{C}_2$ . Catalyst deactivation is most probably associated with unreactive graphite which is formed during the methanation process.

$\text{Fe}_5\text{C}_2$  has been prepared by the reduction of iron oxide in a  $\text{CO}:\text{H}_2$  atmosphere 1:4 between 300 and  $360^\circ\text{C}$  (6). The carbide is isostructural with  $\text{Mn}_5\text{C}_2$ , and a range of solid solutions exist between  $\text{Fe}_5\text{C}_2$  and  $\text{Mn}_5\text{C}_2$  (7). It has been reported (8-10) that nickel carbide  $\text{Ni}_3\text{C}$  and iron carbide  $\text{Fe}_3\text{C}$  are completely soluble in one another, but the stability of the mixed carbide decreases with increasing nickel content.

Bernier (11) observed the beginning of decomposition of  $\text{Ni}_3\text{C}$  on heating between 210 and  $235^\circ\text{C}$ , depending on the previous heat treatment. It was reported by Browning and Emmett (12) that  $\text{Ni}_3\text{C}$  decomposed completely when heated at  $370^\circ\text{C}$  for 24 hours. Furthermore, it was reported by Unmuth et al. (13) that no nickel carbide was observed to form when nickel dispersed on  $\text{SiO}_2$  was heated in a stream of  $3\text{H}_2:\text{CO}$  at  $256^\circ\text{C}$ .

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Supported and unsupported iron-nickel catalysts have been studied by several research groups (13, 14). Raupp and Delgass (14) have indicated that alloys of nickel with iron in approximately equimolar amounts did not form carbides when heated with 3.3 H<sub>2</sub>:CO synthesis gas at 523K for 6 hours. Carbide formation was reported to occur only for iron-rich phases. Unmuth et al. (13) showed that both nickel-poor and nickel-rich iron phases could form carbides. The mixed metal carbides could be stabilized to about 500°C.

There have been no reports concerning the crystallographic or magnetic properties of the system Fe<sub>5-x</sub>Ni<sub>x</sub>C<sub>2</sub>. Since Fe<sub>5</sub>C<sub>2</sub> shows a Curie point at 246°C, any substitution of nickel into the phase could be determined by changes in the Curie point. Furthermore, the optimum solubility of nickel into Fe<sub>5</sub>C<sub>2</sub> could be determined from x-ray diffraction studies of members of the system Fe<sub>5-x</sub>Ni<sub>x</sub>C<sub>2</sub>. Since pure nickel does not appear to carbide under Fisher-Tropsch conditions, it should be present as a separate phase when maximum solubility is achieved.

### Experimental

#### Preparation of Samples

Samples of mixed nickel(II) oxide and iron(III) oxide were prepared by codecomposition of the nitrates [Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, Fisher certified]. Calculated quantities of the nitrates, to give final oxide compositions containing 20 and 33 atomic percent of nickel, were dissolved in water (2 ml/g of sample). The solution was then dried at 150°C for 12 hours, ground, and heated at 400°C for 24 hours.

Two hundred mg of the mixed oxides were then cold pressed at 90,000 psi and the resulting pellets were sieved to a size of 20-60 mesh. In a typical carbide preparation, 0.5g of pellets were loaded into a microreactor (5). The mixed oxides were heated at ambient pressure and a H<sub>2</sub>:CO ratio of 9:1. The gases hydrogen (Matheson, ultrahigh purity), an 81%:19% carbon monoxide:helium mixture (Matheson > 99.99%), and argon (Matheson, ultrahigh purity) were used as supplied. The system was initially purged with argon at room temperature and the sample was then heated to 290°C for 45 minutes under a 60 cm<sup>3</sup>/min flow of argon. The reaction was then carried out with a 9H<sub>2</sub>:CO gas mixture (60 cm<sup>3</sup>/min) at ambient pressure for 60 hours. At the end of this time the product was characterized by x-ray diffraction analysis and its magnetic susceptibility as a function of temperature was determined.

In order to properly characterize the carbides formed, their crystallographic and magnetic properties were compared to those of a mechanical mixture of nickel metal and pure Fe<sub>5</sub>C<sub>2</sub> (0.5 mol Ni + 0.1 mol Fe<sub>5</sub>C<sub>2</sub>). The nickel metal was obtained by reducing NiO with carbon monoxide and hydrogen (1:9) mixtures at 290°C for 24 hours. Pure Fe<sub>5</sub>C<sub>2</sub> was prepared by heating α-Fe<sub>2</sub>O<sub>3</sub> with carbon monoxide and hydrogen (1:9) at 290°C for 24 hours. The final mixture was obtained by mixing the two end products in the desired mole ratios.

#### X-Ray Analysis

X-ray powder patterns of the samples were obtained using a Philips diffractometer and monochromated high intensity CuKα<sub>1</sub> radiation (λ = 1.5405Å).

The diffraction patterns were taken in the range  $12^\circ < 2\theta < 80^\circ$  with a scan rate of  $1^\circ (2\theta) \text{ min}^{-1}$  and a chart speed of 30 in  $\text{h}^{-1}$ .

The nickel (200) x-ray diffraction peak overlaps a cluster of three unresolved peaks in the  $\text{Fe}_5\text{C}_2$  pattern. Consequently, analysis of the concentration of nickel can only be achieved by using a pattern-fitting procedure. In such a procedure, "standard" nickel and  $\text{Fe}_5\text{C}_2$  patterns are adjusted and combined in various proportions to construct "trial" patterns; the trial patterns are compared with the experimental pattern, and the phase concentrations are deduced from the best fit.

The most reliable "standard" patterns are those obtained experimentally from samples of the pure phases. Accordingly, slow x-ray scans at  $0.25^\circ (2\theta) \text{ min}^{-1}$  were taken over the range  $49^\circ < 2\theta < 54^\circ$  for both pure nickel and pure  $\text{Fe}_5\text{C}_2$ . These were digitized using a HP 7225A plotter to yield standards suitable for computer processing.

A computer program (written in Microsoft Basic and compiled) has been developed (15) which employs the simplex method (16) to achieve a least-squares fit of a digitized x-ray pattern using experimental standard patterns for two possible phases. A close fit to the pattern for a 50 at% nickel/ $\text{Fe}_5\text{C}_2$  mechanical mixture was obtained and served to calibrate the intensity of the standard nickel peak against the  $\text{Fe}_5\text{C}_2$  standard.

#### Determination of Curie Points

Curie points for members of the series  $\text{Fe}_{5-x}\text{Ni}_x\text{C}_2$  as well as the mechanical mixtures of metallic nickel and  $\text{Fe}_5\text{C}_2$  were made using a Faraday balance (17) equipped with a high temperature heater. In order to prevent any decomposition, the samples were transferred from the microreactor under argon to a glove box where they were put into small glass bubbles, evacuated and sealed. The sealed samples were heated in an atmosphere of 40 torr helium from room temperature to  $500^\circ\text{C}$  at a rate of  $30^\circ/\text{min}$ . The relative magnetization (at a constant field strength of 100 Oe) was recorded as a function of temperature using a Bascom-Turner Acquisition Center, Model 4110.

#### Results and Discussion

Samples of  $\text{Fe}_5\text{C}_2$ , 20 and 33 atomic percent nickel substituted  $\text{Fe}_{5-x}\text{Ni}_x\text{C}_2$  were prepared by the codecomposition of iron-nickel nitrates followed by reduction in a 9:1 hydrogen:carbon monoxide atmosphere. The relative magnetization as a function of temperature for these samples is plotted in Fig. 1. Included in the figure is the magnetization of a 1:1 mechanical mixture of  $\text{Fe}_5\text{C}_2$  and metallic nickel. From Fig. 1 it can be seen that the 33 atomic percent nickel sample has lowered the Curie point of  $\text{Fe}_5\text{C}_2$  from  $250^\circ\text{C}$  to  $230^\circ\text{C}$ . It is also evident that not all of the nickel substituted for iron in this sample. It appears that the optimum substitution of nickel for iron in  $\text{Fe}_5\text{C}_2$  under the conditions of preparation resulted in the composition  $\text{Fe}_4\text{NiC}_2$ .

These results were corroborated by the x-ray diffraction study. In Fig. 2, it can be seen that the 33 percent substituted nickel sample can best be fitted to the diffraction peaks assuming a 20% nickel substituted phase and metallic

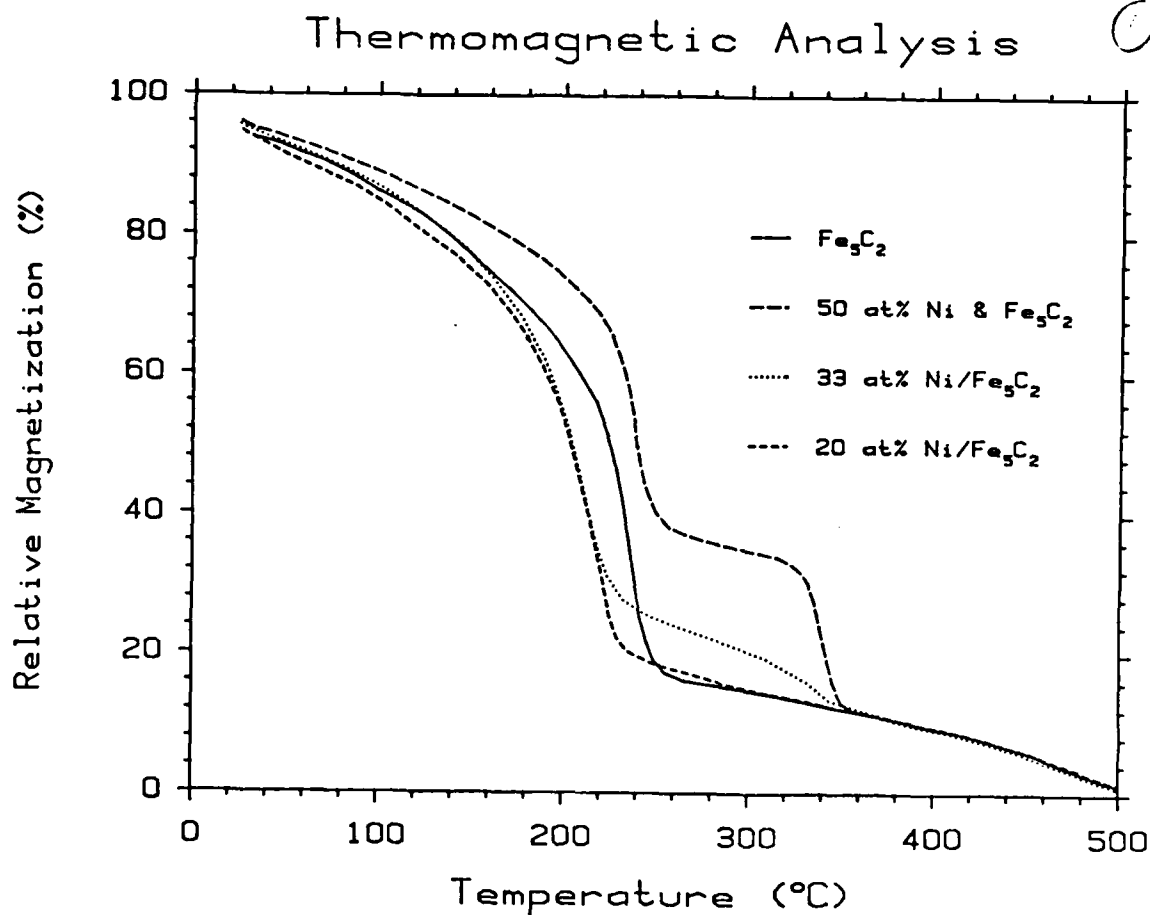


FIG. 1

Variation of magnetization with temperature, showing the shift in Curie temperature between pure  $\text{Fe}_5\text{C}_2$  and reacted Ni/ $\text{Fe}_5\text{C}_2$  samples. The curve for a 50 at% mechanical mixture of Ni and  $\text{Fe}_5\text{C}_2$  is included for comparison.

nickel. These results confirm the magnetic data which indicated an optimum substitution corresponding to the stoichiometry  $\text{Fe}_4\text{NiC}_2$ . For a 25 atomic percent nickel sample, there was clear evidence for the presence of metallic nickel.



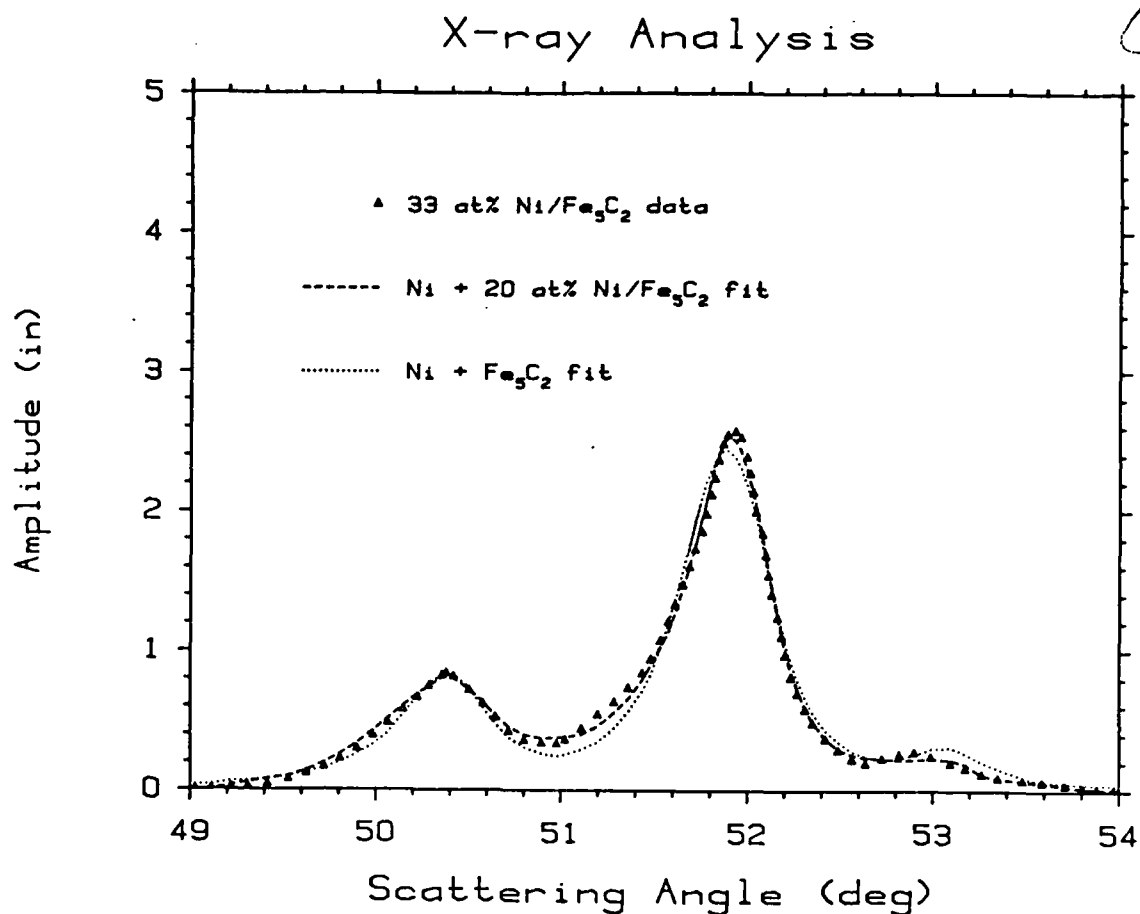


FIG. 2

X-ray pattern of a reacted 33 at% Ni/Fe<sub>5</sub>C<sub>2</sub> sample. The fitted curves based on Ni + Fe<sub>5</sub>C<sub>2</sub> and on Ni + 20 at% Ni/Fe<sub>5</sub>C<sub>2</sub> are shown for comparison.

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